Degradation of superconductivity and spin fluctuations by electron over-doping in $LaFeAsO_{1-x}F_x$

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Low energy spin fluctuations are studied for the electron-doped Fe-based superconductor $LaFeAsO_{1-x}F_x$ by inelastic neutron scattering up to the energy transfer of $\omega = 15$ meV using polycrystalline samples. Superconducting samples ($x = 0.057, T_c = 25$ K and $x = 0.082, T_c = 29$ K) show dynamical spin susceptibility $\chi"(\omega)$ almost comparable with the parent sample's. However $\chi"(\omega)$ is almost vanished in the $x = 0.158$ sample where the superconductivity is highly suppressed. These results are compatible with the theoretical suggestions that the spin fluctuation plays an important role for the superconductivity.

KEYWORDS: Superconductivity, Spin fluctuation, Inelastic neutron scattering, Iron pnictide superconductor, $LaFeAsO_{1-x}F_x$.

1. Introduction

Magnetic fluctuation has been expected to be a candidate as the origin of the Cooper pair formation in the high transition temperature (high-T_c) superconductivity since it appears with antiferromagnetic (AF) instability in the high-T_c cuprates.[1)] Strikingly, recently-discovered new class of Fe-pnictide high-T_c superconductor $LaFeAsO_{1-x}F_x$[2)] and family compounds show superconductivity just beside the AF regime in the $T - x$ phase diagram.[3,4)] Moreover the AF spin fluctuations have been observed by neutron scattering below T_c for the superconducting 122[5–9)] and 11 compounds.[10,11)] This similarity has drawn much attention to the new Fe-pnictide superconductors which give a unique opportunity to study the correlation between the AF spin fluctuation and the high-T_c superconductivity.

LaFeAsO, a parent compound of the 1111-type Fe-pnictide superconductors, is an AF metal. Band calculations indicate there are cylindrical Fermi surfaces of holes and electrons at Γ- and M-points, respectively.[12)] Nesting between them induces 2-dimensional (2D) AF spin fluctuations that have been observed by inelastic neutron scattering near $\mathbf{Q}^{2D}_{AF} = (1/2, 1/2, 0) = 1.10$ Å^{-1} in the tetragonal notation.[13)] Then, a 3-dimensional (3D) AF order develops below $T_N = 137$ K with AF propagation vector $\mathbf{Q}^{3D}_{AF} = (1/2, 1/2, 1/2)$.[14)] Substitution of oxygens by fluorine atoms and/or introducing oxygen vacancies provides electrons into the system. The AF order is suppressed by ~ 4 % of F-doping and beyond this doping level the system shows superconductivity (Fig. 1(a)).

From the early stage of the Fe-based superconductors research, many authors have pointed out the importance of spin fluctuations arising from the Fermi surface nesting in realizing the superconductivity.[15–20)] Although the spin fluctuations have been observed in the superconducting 122 and 11 compounds, study of spin fluctuations of the 1111 system is very sparse due to the difficulty in synthesizing high quality samples. The nuclear magnetic resonance (NMR) study of the $LaFeAsO_{1-x}F_x$ system shows that the spin fluctuations near $\omega = 0$ dramatically decrease as doping increases up to $x = 0.10$ whereas the T_c changes only little.[21)] Apparently this behavior indicates weak coupling between the spin fluctuation and the superconductivity. To reconcile these facts and clarify if the spin fluctuation plays a crucial role, a systematic study of spin fluctuations is desirable for the $LaFeAsO_{1-x}F_x$ system up to the overdoped region where the superconductivity is suppressed. For above purpose, we have performed inelastic neutron scattering on $LaFeAsO_{1-x}F_x$ with x=0.057 ($T_c = 25$ K), $x = 0.082$ ($T_c = 29$ K), and overdoped $x = 0.158$ (superconductivity is highly suppressed).

2. Experimental details

Powder samples of $LaFeAsO_{1-x}F_x$ have been synthesized by solid state reaction starting with nominal compositions of $x = 0.05, 0.10$, and 0.20. The x values of the synthesized samples were determined by secondary ion-microprobe mass spectrometry to be 0.057(3), 0.082(5), and 0.158(7), respectively. Powder x-ray diffraction data show that our samples contain only single 1111 phase with space group of $P4/nmm$ ($a = 4.0$ Å, $c = 8.7$ Å), demonstrating the high quality of the samples. Superconductivity of the prepared samples was characterized by SQUID measurements. Figure 1(b) indicates Meissner signals for the three samples measured in a cooling process under a magnetic field of 5 Oe. T_c is characterized as an onset temperature of the Meissner signal and plotted

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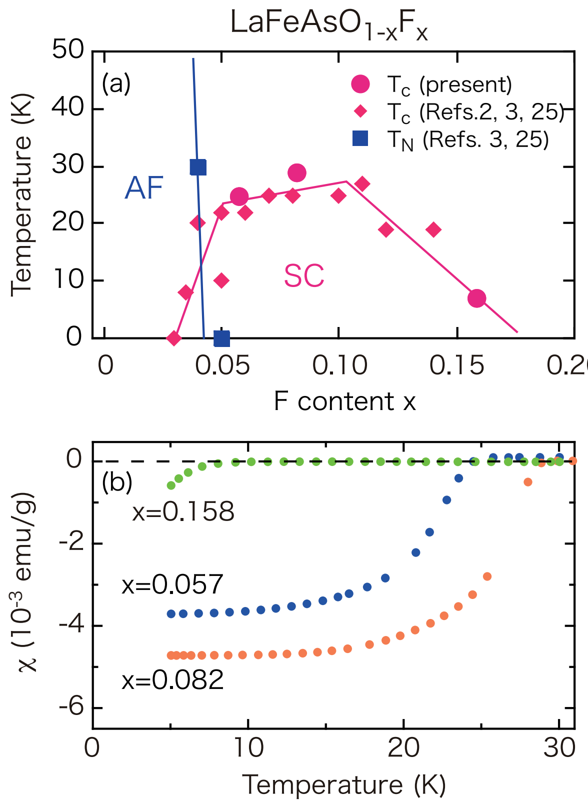

Fig. 1. (Color online) (a) $x-T$ phase diagram of $LaFeAsO_{1-x}F_x$. Circles represent T_c of the present samples. Diamonds and squares indicate T_c and T_N, respectively, adopted from previous works.[2,3,21] (b) Meissner signals of the present polycrystalline samples measured in a cooling process under a magnetic field of 5 Oe.

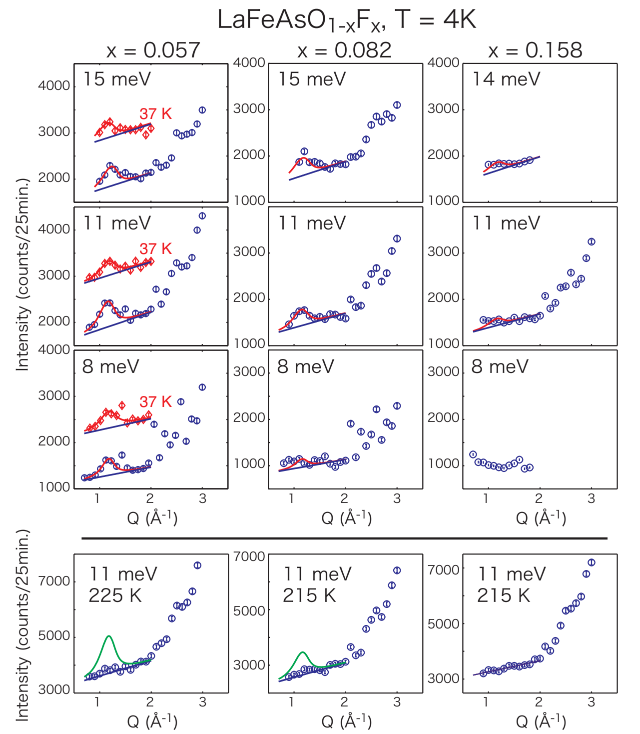

Fig. 2. (Color online) Neutron scattering profiles scanned as a function of momentum transfer Q with fixed energy transfers $\omega = 8, 11$, and 15 meV. The top 9 panels show data at 4K, and the bottom 3 panels indicate data of $\omega = 11$ meV at ~ 220 K. In the data panels of the $x = 0.057$ sample, data at 37 K ($> T_c$) are also shown. They are shifted by 1000 counts for clarity. Solid lines in the top panels are fits to a resolution-convoluted Lorentzian function on sloped background. Solid lines in the bottom panels show the expected intensity in case that the intensity at 4 K is phonon.

in Fig. 1(a) by circles together with T_c and T_N reported in previous works. T_c of the $x = 0.057$ and 0.082 samples agree well with previous reports. By neutron diffraction we confirmed that all samples exhibit no AF order down to 4 K. The overdoped $x = 0.158$ sample shows $T_c = 7$ K, nevertheless it has a low volume fraction of about 10 % at 5 K. Thus, the superconductivity of this sample is highly suppressed.

Inelastic neutron scattering experiments were performed using the triple-axis spectrometer TAS-1 installed at the research reactor JRR-3 of Japan Atomic Energy Agency. Powder samples of ~ 25 g for each composition were used. Collimation sequence of open-80′-S-80′-80′ (S denotes sample) and fixed final neutron energy at $E_f = 30.5$ meV were utilized. Inelastic measurements were done on the neutron energy loss condition. This configuration gives instrumental resolutions of 3.5 meV in energy and 0.06 Å^{-1} in momentum transfer. Volume ratios were estimated by nuclear Bragg intensities at $(0, 0, 2)$ normalized to x-dependent structure factor.[22] So obtained volume ratios of the samples with $x = 0.057$, 0.082, and 0.158 were 1.0: 0.8 : 1.1.

3. Results

Figure 2 shows neutron scattering intensity as a function of momentum transfer Q. The intensity increases as Q increases due to the Q^2-dependence of phonon scattering. We focus on the expected magnetic scattering near $Q_{AF}^{2D} = 1.1$ Å^{-1}. Data of $x = 0.057$ at 37 K which is above T_c are also shown. Solid lines of the 4 K and 37 K data are the results of fits of the data in the range of $Q \leq 2$ Å^{-1} to a resolution-convoluted Lorentzian function. Since the magnetic excitation is very steep against Q in the energy range of $\omega \leq 15$ meV,[13] we assumed the magnetic peak position Q_{AF} to be independent of ω. The background level, which comes from mostly phonon contribution, is also adjusted as a sloped background. (Adjusted backgrounds are also shown in Fig. 2.)

It is shown that the $x = 0.057$ sample shows clear peaks at all energies at both 4 K and 37 K. Data at 11 meV shows clear enhancement at 4 K. Existence of the magnetic peaks at 37 K evidences that the superconducting $x = 0.057$ sample has spin fluctuations even above T_c. The $x = 0.082$ sample also shows peaks at 11 and 15 meV, although the peak structure at 8 meV is somewhat unclear. The fittings for all these peaks give $Q_{AF} \sim 1.15$ Å^{-1} which is close to Q_{AF}^{2D} and consistent with that observed for the parent compound for $T > T_N$.[13] These peaks are gone at high temperatures. Data at 11 meV at $T \sim 220$ K are shown as representative high-T data in the lower panels of Fig. 2. The solid lines are peak profiles calculated by assuming that the peak observed at 4K is phonon contribution: that is, it

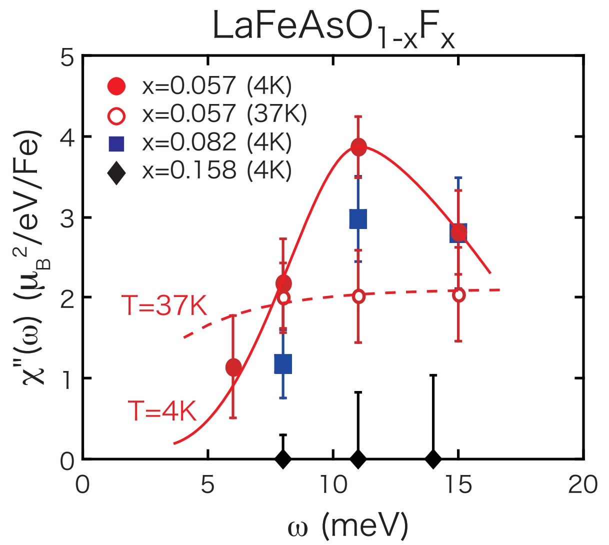

Fig. 3. (Color online) Imaginary part of dynamical spin susceptibility $\chi''(\omega)$ at 4 K calculated by normalizing to an incoherent scattering of standard vanadium. Data at 37 K ($> T_c$) of the $x = 0.057$ sample are also shown by open circles. The error bars of data for only $x = 0.158$ represent maximum values estimated by fitting with fixed backgrounds that are the same as those of $x = 0.082$. The solid and dashed lines are a guide to the eyes.

depends on the temperature by $n(\omega) + 1$, where $n(\omega)$ is the Bose factor $(e^{\omega/k_BT} - 1)^{-1}$. The profiles can not reproduce the observed data at all, indicating that the observed peaks are indeed magnetic.

In contrast with these two samples, the overdoped $x = 0.158$ sample shows no clear magnetic peaks at all energies at both low and high temperatures. The fitting procedure to the $x = 0.158$ data with float parameters results in a nearly zero magnetic intensity. The solid lines of the 4K data are the results of fits by assuming the same background, peak position and width as those of $x = 0.082$ to estimate maximum intensity of magnetic scattering. Nevertheless, the intensity is still very small. These facts evidence that the $x = 0.158$ sample has no spin fluctuations in this energy range.

We have calculated absolute values of Q-integrated $\chi''(\omega)$ at 4 K by normalizing the magnetic cross sections to the incoherent scattering cross section of standard vanadium. Results are summarized in Fig. 3. For the data of $x = 0.158$, error bars represent the maximum values of $\chi''(\omega)$ estimated from the fore-mentioned fitting. The superconducting samples of $x = 0.057$ and 0.082 have maximum at $\omega \sim 11$ meV at 4 K, corresponding to $\sim 4.7 k_BT_c$. Comparison to the spectrum of $x = 0.057$ at 37 K clarifies that the maximum appears due to the enhancement below T_c. For the $x = 0.158$ sample, the $\chi''(\omega)$ is suppressed even at 11 meV. This demonstrates the suppression of the spin fluctuations in the energy range up to 15 meV. We summarize x-dependence of $\chi''(\omega)$ in Fig. 4. In the figures of $\omega = 8$ and 11 meV, $\chi''(\omega)$ of the parent compound are also presented by open symbols. These are measured with the same spectrometer configuration using the identical sample reported in Ref. 13). The spin fluctuations in the $x = 0.158$ sample is highly suppressed, whereas those of the superconducting $x = 0.057$ and 0.082 samples are comparable to those of the parent compound. Thus, an appreciable amount of spin fluctuations survives in the energy range of $\omega \leq 15$ meV in the superconducting samples.

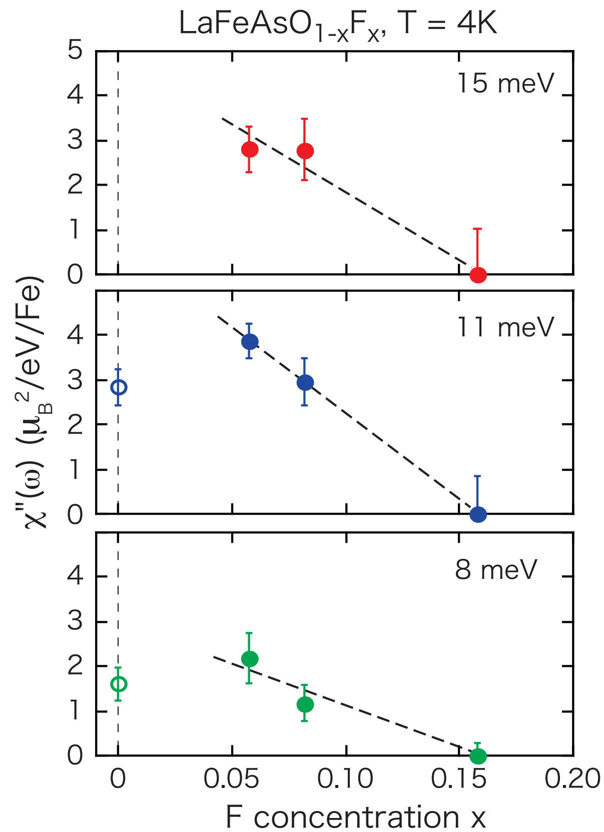

Fig. 4. (Color online) Imaginary part of dynamical spin susceptibility $\chi''(\omega)$ at $\omega = 8, 11$, and 15 meV as a function of F content x. Open symbols show $\chi''(\omega)$ of the parent compound measured at just above the Néel temperature 140 K, where the $\chi''(\omega)$ is maximum.

4. Discussion

We have shown that the spin fluctuation in $LaFeAsO_{1-x}F_x$ becomes suppressed by electron-overdoping at 4 K. It is reported that the superconducting Fe-122 and 11 systems show the enhancement of the spin fluctuation at energy transfer of $4.2 \sim 5.3\ k_BT_c$ below T_c observed by neutron scattering.[5–11] We have observed qualitatively similar enhancement for the present 1111 sample with $x = 0.057$ at 11 meV ($\sim 5.1\ k_BT_c$). This feature has been explained by either $s_\pm$ scenario due to the superconducting gap symmetry,[26,27] or simple s_{++} scenario due to the redistribution of spectral weight by the gap opening.[28] Distinguishing these two requires more detailed measurements and which is not the main scope of this Letter.[23] Instead we put emphasis on the suppression of the magnetic fluctuation in the overdoped sample.

The present $x = 0.057$ sample shows well defined spin fluctuation above T_c demonstrating the existence of the bare spin fluctuations without the enhancement below T_c. The disappearance of the magnetic signal in

$x = 0.158$ at 4 K evidences the disappearance of the bare spin fluctuations. It is reasonable that the hole Fermi surface at the Γ-point shrinks by electron doping and eventually disappears by over-doping. This results in a poor nesting condition to the electron Fermi surface at the M-point and a suppression of the spin fluctuations. Recent ARPES measurements on $BaFe_{2-x}Co_xAs_2$, where the Co-doping supplies electrons, suggest a bad nesting condition due to the shrinkage of the hole Fermi surface in a non-superconducting over-doped sample.[24)] In addition, neutron measurements of overdoped $BaFe_{2-x}Co_xAs_2$ shows suppression of the inelastic magnetic scattering, consistent with our results.[25)]

We cannot rule out the possibility that the magnetic scattering in the $x = 0.158$ sample still exists at lower Q, which is not accessible in the present configuration. However the scattering near $Q = 1.1$ Å^{-1} disappears clearly, which corresponds to the nesting vector from the Γ to M points. These facts imply the importance of the Fermi surface nesting between the Γ and M points for the superconductivity in the Fe pnictides. The nesting should induce elementary fluctuations which may act as a source of the superconductivity, such as spin, orbital, and charge fluctuations. So far, only the spin fluctuation has been observed to disappear at the overdoped regime. Although this is not a direct evidence of spin driven superconductivity, but it is an implication of the coupling between the spin fluctuation and the superconductivity.

Finally, we mention a difference of the spin fluctuations probed by the present study and NMR. Our neutron measurement shows that an appreciable amount of $\chi"(\omega)$ which is comparable to that of the non-doped sample is present in the superconducting samples with $x = 0.057$ and $x = 0.082$. In contrast, NMR-$1/T_1T$ measurement on this system revealed that the spin fluctuation in the low energy region which is much lower than that of our neutron measurement is suppressed by small doping.[21)] In our measurements, the peak structure clearly observed in $x = 0.057$ at 8 meV becomes somewhat unclear in $x = 0.082$. Even lower energy region may show a drastic decrease of $\chi''(\omega)$ with doping. Clearly the lower energy measurements of neutron scattering at temperature range above T_c are necessary using single crystals.

5. Summary

Systematic neutron scattering study of $LaFeAsO_{1-x}F_x$ revealed that the spin fluctuations up to 15 meV that are comparable to the non-doped LaFeAsO survive in the superconducting samples with $x = 0.057$ and 0.082, whereas they are highly suppressed in the over-doped $x = 0.158$ where the superconductivity is also highly suppressed. This can be understood by a disturbed nesting condition due to the reduction of the hole-Fermi surface at the Γ-point upon electron over-doping. Our observation is compatible with theoretical suggestion that the spin fluctuations due to the Fermi surface nesting is important for the iron-pnictide superconductivity.

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